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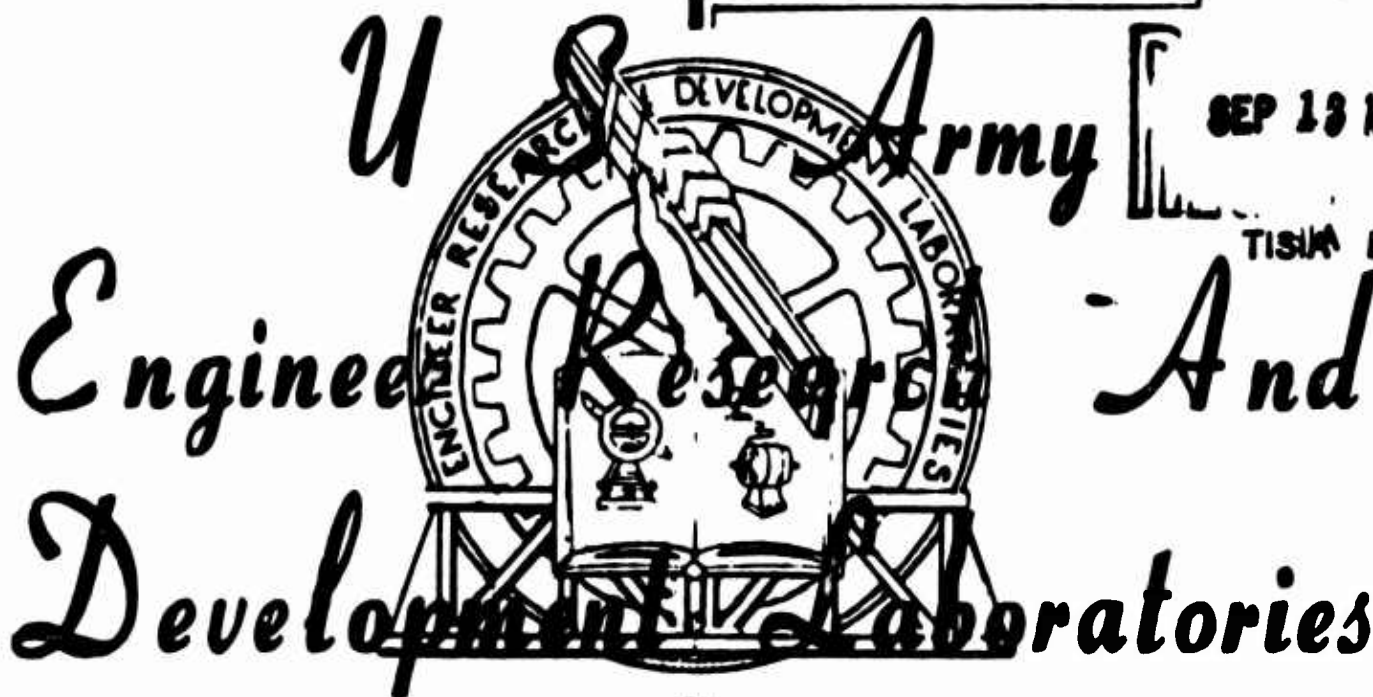
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EXPLOSIVE PROPERTIES OF INITIAL EXPLOSIVES
CRYSTALLOGRAPHIC, MODECULAR, AND
QUANTUM-CHEMICAL CONSIDERATIONS

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EXPLOSIVE PROPERTIES OF INITIAL EXPLOSIVES

CRYSTALLOGRAPHIC, MOLECULAR, AND QUANTUM CHEMICAL CONSIDERATIONS

Akira Suzuki

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EXPLOSIVE PROPERTIES OF INITIAL EXPLOSIVES: PRIMARILY CRYSTALLOGRAPHIC-, MOLECULAR STRUCTURAL- AND QUANTUM-CHEMICAL CONSIDERATIONS

Akira Suzuki

I. A HISTORICAL REVIEW OF STUDIES ON EXPLOSIVE PROPERTIES OF INITIAL EXPLOSIVES

1. Impact Sensitivity of Initial Explosives

Impact sensitivity is one of the most remarkable characteristics of explosives. A great number of measurements have been reported on this sensitivity. But, the measured values of one type of explosives vary with the measurer and the place of measurement, and have little or no assurance of recurrence. Only few reports treat theoretical explanation of the sensitivity. W. Taylor (ref. 1) in 1932, and Arami (ref. 2) in 1939, proposed their theoretical formulas of sensitivity, respectively, explored the relationships between the heights of fall of falling weights and temperatures for various types of explosives, and rational-ized their theoretical formulas. In both cases, the tests were con-ducted within small temperature ranges above the normal temperature. From the degree of accuracy of their sensitivity values, it is unrea-sonable to determine the sensitivity curves. If measurements can be taken at considerably low temperatures, it would be interesting, because we can then determine which of these formulas is more universally appli-cable. Furthermore, it would be interesting, for few measurements, if any, have been taken of the sensitivity at low temperatures in the study of explosives in the past.

Taylor went further to explain the mechanism of impact explosion of initial explosives by the tribochemical theory (ref. 3). According to this theory, it is expected that a fine powder form of any initiator, having therefore much more area, has greater sensitivity than a rougher crystal grain form of the same initiator.

2. Thermal Sensitivity of Initial Explosives

Thermal sensitivity, or so-called ignition point, is one of the important characteristics of explosives. From olden times, many students

have treated of phenomena of explosion by heating (ref. 4). Patry (ref. 5) confirmed the following from pictures taken by the chronographic method:

(1) The explosive decomposition caused by a terrific impact (detonator) is invariably a fulminating explosion.

(2) The explosive decomposition caused by a temperature rise (flame) is a combustion in the case of mercury fulminate, and a fulminating explosion in the case of lead azide. Consequently, initial explosives can be classified into the following two categories according to the nature of explosion caused by the rise in temperature:

(a) those similar in nature to mercury fulminate;

(b) those similar in nature to lead azide.

As the measurement data of the impact sensitivities and ignition points of various types of explosives increase, attempts naturally are made to consolidate these to find some universal rules about them.

A great deal of measurements of impact sensitivities and ignition points of initial explosives have been reported by L. Woehler (ref. 6), Taylor and Rinkenbach (ref. 7), and others, but no conclusion as to rules has been drawn from these data.

3. Considering the Explosion Mechanism from the Viewpoints of Reaction Speed and Crystal Structure

As the explosion of initial explosives takes place instantaneously, /143 it is difficult to take out quantitative values from this phenomenon. Therefore, Garner, et al. (ref. 8) attempted to control the speed by some method or other in order to make the measurement possible. They succeeded in this effort to some extent. That is, they began their study with the thermal decomposition of mercury fulminate at temperatures lower than its ignition point, and worked up in temperature past the ignition point to explore the mechanism of explosion at temperatures above the ignition point.

They assumed that Smekal's cracks and blocks exist in the crystal of mercury fulminate, and that the chain reaction as seen in the thermal decomposition of mercury fulminate is a ramose type, made possible by the arrangement of mercury fulminate ions in the crystal whereby the decomposition of one ion exposes two or more ions.

They assumed further that the chance of thermal decomposition developing into explosion occurs when the two mercury fulminate ion layers on the surfaces of two adjacent Smekal's blocks decompose

simultaneously. But they did not experimentally ascertain whether or not mercury fulminate has such a structure. It is known that potassium azide has exactly such an arrangement as a result of analyses of its crystal structure. The similarity between the fulminic acid ion and the azide ion is such that what can happen to azides can happen to fulminates too. Therefore, they expressed the opinion they could assume that mercury fulminate also has such a convenient structure.

However, N. Seménoff (ref. 9) critizes Garner's argument as follows. The reason why Garner had to make the foregoing assumption is the fact that he held the final product of the reaction responsible for the catalytic action in the thermal decomposition reaction. One of the weaknesses of his assumption is its artificiality. If we assume the catalytic action is performed by an intermediate product which decomposes relatively rapidly, but yet is comparatively stable, we can eliminate such complexities as Garner's theory has.

Let us consider these two schools of theories. Seménoff, while he assumed the catalytic action of an intermediate product, failed to prove the existence of such an intermediate product after all his efforts. Neither could he explain the phenomenon that the mercury fulminate crystal, when heated up to the acceleration period and when more than 1/5 of it decomposes, can no longer explode. On the other hand, Garner introduced new crystallographic knowledge, made microscopical observations, and gave us some clues for further clarification of various facts. Therefore, if we proved by experiment what he failed to prove, and what Seménoff criticized him as being artificial about, we would be able to go a long way toward clarifying the thermal decomposition and the mechanism of explosion of mercury fulminate. Thus, we bring into focus the questions of crystal structure and molecular arrangement in the crystal of initial explosives.

Among azides, analyses of crystal structure have been conducted for ammonium (ref. 10), potassium and sodium (ref. 11), rubidium (ref. 12), thallium (ref. 13), cyanurictriazide (ref. 14), etc. In 1927, Guenter and his associates (ref. 15) maintained that by analyzing the crystal structure of azides of various metals, and by systematically measuring the differences in interatomic distance, they would be able to explain reasonably the sensitivities of these salts. They set about their study, but the structural analysis itself proved to be so difficult that they could not succeed after all. In 1931, F. D. Miles (ref. 16) studied the crystallographical forms of mercury fulminate, lead azide and lead trinitroresorcinol, and at the same time measured the sizes of unit cells and numbers of molecules in those cells by use of X-rays.

However, such information on crystal structure is inadequate as the basis for clarification of the mechanism of explosion.

The increased sensitivity of initial explosives has been vaguely but solely attributed to the molecular strains that developed during the formation of the crystal. However, little evidence has been offered in support of this from the standpoint of crystal structure. Furthermore, in the light of the theory of crystal growth, it is highly inconceivable that molecules be unduly strained during the growth of a crystal.

Subsequent to the foregoing considerations, we must again go back to the old thermochemical explanation that the reason for the high sensitivity of initial explosives is the fact that they are products of endothermic reactions and are therefore unstable.

4. Quantum-Chemical Considerations of Explosive Properties

Meanwhile, L. Pauling (ref. 17) introduced the concept of quantum resonance into the field of initial explosives, and originated the trend of considering the explosive properties of initial explosives quantum-chemically.

Since a fair amount of knowledge of his theory is necessary to follow my discussion, I will elaborate on this in more detail.

In the ionic crystal as found in such azides as potassium or sodium azide, the azide ions are placed symmetrically on a straight line, and the terminal atoms are at a distance of 1.15 ± 0.02Å from the center atom. Let us assume now that the following three structures: A, B and C resonate and that

$$A. \quad R - \ddot{N} = \overset{+}{N} = \ddot{N}^-$$
$$B. \quad R - \ddot{N}^- - \ddot{N} \equiv N:$$
$$C. \quad R - \ddot{N} \equiv N^+ - \ddot{N}^-$$
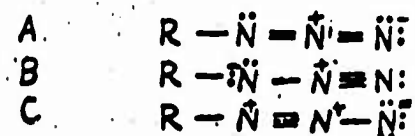
make the same degree of contribution. Then, the interatomic distance

becomes 1.15Å, which is the exact value obtained in experiments. On the other hand, if we consider structure A only, we arrive at such a poor

value as 1.22Å.

Meanwhile, the structure of methylazide, a covalent bond molecule, is considered to be

$$H_3C - N \xrightarrow{1.24 Å} N \xrightarrow{1.10 Å} N$$
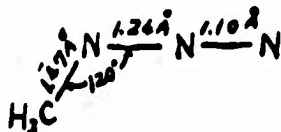
(The probable errors in these distances are about 0.02Å.) The covalent bond type azide groups of cyanurictriazide, triazohydroacid, etc., show

similar atomic arrangements, and the two N-N distances are 1.26Å and

1.11Å in the former case, and 1.24Å and 1.13Å in the latter case. These results do not agree with the resonance among the following three struc- /144 tures, A, B and C.

A $\ddot{N} - \dot{N} - \ddot{N}$
B $\ddot{N} - \dot{N} = N$
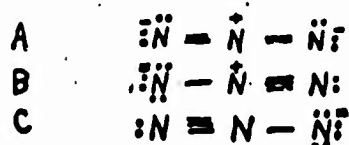C $N \equiv N - \ddot{N}$

However, if we eliminate C and assume that A anb B resonate with each

other to the same extent, the calculated values become 1.24Å and 1.12Å, respectively, and coincide very well with the measured values. The fact that structure C cannot exist clarifies the significance of the rule of adjacent electric charge.

Furthermore, by referring to this rule, we can explain the large difference in stability existing between the covalent type and the ionic type azides. The covalent type azide resonates between the two types of structures, and its resonance energy is in the order of 25 kcal/mol (carboxyl group, etc.). The resonance energy of the ionic type azide among the three types of structures is about 45 kcal/mol. Therefore, the covalent type azide is about 20 kcal/mol more unstable. From this, it can be explained that, while azides of heavy metals are extremely explosive, those of alkali and alkaline earth metals are so stable as not to explode until heated to high temperatures.

II. THE SYNTHESIS AND PREPARATION OF INITIAL
EXPLOSIVES USED IN THE EXPERIMENT

I will just mention the names of distributors for the items commercially marketed, and the source of information for the items synthesized in accordance with the methods described in the literature.

1. Fulminates

(1) Mercury fulminate

(a) Crude mercury fulminate: Purchased from Nippon Chisso K K (Japan Nitrogen Company, Ltd.), Appearance: light yellowish brown. Purified to 97.10 percent by the sodium thiosulfate method.

(b) White mercury fulminate: Dissolve crude mercury fulminate in concentrated aqueous ammonia (28 percent concentration), and pour it into a water solution of acetic acid (5 percent concentration) until neutralized. Separate the sediment by filtration and rinse it. 99.42 percent purity.

(c) Powder mercury fulminate: Place a small amount of crude fulminate into an agate mortar, soak it in distilled water, and grind it for about 5 minutes. Then, separate it by filtration and dry it.

(d) Single crystal mercury fulminate: In a white diamond-shaped plate crystal, whose size is between 1 and 1.5 mm, it was synthesized as follows: dissolve crude mercury fulminate in concentrated aqueous ammonia (28 percent concentration) and filter it. Pour the filtrate into a water solution of acetic acid (0.1 percent) until it turns slightly basic. Keep it in a dark, quiet place for several days to allow the above-mentioned crystal to form. Initially, I tried the method described in F. D. Miles' (ref. 18) report, but did not succeed.

(2) Silver fulminate (ref. 19): White needle crystals with a silky luster. Not very sensitive to light.

(3) Potassium fulminate (ref. 20): White sheet crystals.

2. Azides

(1) Lead azide: Drop a water solution of lead acetate into a water solution of hydrozoic acid to obtain a white sediment. Separate the sediment by filtration and dry it. Exercise care not to expose it to light. Lead content is 70.9 percent.

(2) Silver azide: Drop a 5 percent silver nitrate water solution into a 2 percent sodium azide water solution while stirring it briskly. In the suspension thus created, it forms a cheese-like sediment. Separate the sediment by filtration and dry it. When exposed to light, it turns dark purple.

(3) Potassium azide: A double decomposition of a calculated amount of barium nitride and a calculated amount of potassium sulfate was effected to obtain pure potassium azide. Eliminate by filtration the white sediment of barium sulfate that forms as a result of the double decomposition. Vacuum distill the filtrate to remove most of the water. Evaporate the residual solution on a water heater, and cool it to precipitate crystals. Recrystallize the crystals.

3. Lead Trinitroresorcinol (ref. 21)

Appearance: yellowish brown transparent columnar crystals. 99.8 percent purity. (Lead content: 44.1 percent; theoretical content: 44.2 percent).

(1) Crystalline lead trinitroresorcinol: By the method of synthesis previously mentioned, pour the lead nitrate water solution more gradually, and stir more slowly, in order to obtain perfectly crystalline granules.

(2) Powder lead trinitroresorcinol: Pulverize the above-mentioned crystalline granules in the manner by which powder mercury fulminate is ground. Separate it by filtration and dry.

(3) Anhydrous lead trinitroresorcinol (ref. 22): Put lead trinitroresorcinol into a vacuum container, and heat and dehydrate it for about two hours in a thermostatic bath, while drawing air with a vacuum pump.

4. Silver Acetylide (ref. 23)

Appearance: gray silvery white crystals.

5. Tetracene (ref. 24)

Appearance: light yellow crystalline powder.

6. Diazodinitrophenol (ref. 25)

Appearance: shiny yellowish brown columnar crystals.

7. Lead Picrate

In the same manner as described for lead trinitroresorcinol, drop lead acetate water solution into a water solution of picric acid, and condense it by heating to obtain yellow columnar crystals.

8. Cyanates

Cyanates are not initial explosives. However, they were used for the purpose of comparing them with, and thus facilitating the clarification of the explosive properties of, fulminates and azides.

(1) Silver cyanate: In the same manner as described for silver azide, dissolve potassium cyanate in water, and drop the solution immediately into a silver nitrate water solution, to obtain a sediment

similar in appearance to silver azide. At forming, the sediment is white, but it soon turns light yellow.

(2) Potassium cyanate (ref. 26): White needle crystals.

III. THE IMPACT SENSITIVITY (MAINLY IN LOW TEMPERATURE RANGE) OF INITIAL EXPLOSIVES

1. Equipment and Method of Experiment

(1) Silver sand tester. This is an apparatus whereby a falling weight (steel ball) falls perpendicularly and strikes a steel pellet and a sample placed between the layers of sand in a copper cup.

(a) Falling weight suspension device. Utilizing an electric magnet, it discharges all residual magnetism at the time of the falling of the weight.

(b) Falling weight, made of special steel:

Weight (g)	Diameter (mm)
28.15	21.5
16.27	16.5

(c) Copper cup. Inside diameter, 3 mm; depth, 3 mm; thickness, 0.5 mm.

(d) Steel pellet. Shore scleroscope reading, 60 – 40). Diameter, 5.6 mm; length, 9 mm; shape, cylindrical.

(e) Sand. Standard sand for testing cement. Under sieve mesh, 20, and over sieve mesh, 35. Smooth-surfaced grain.

(2) Low temperature thermostatic room. We used a low temperature test room (frontage, 6 m; depth, 4 m; height, 4 m) in the low temperature, low pressure laboratories in the Naval Aviation Arsenal. Men were in the room while the experiment was being conducted. The temperature error during the experiment was $\pm 0.5^{\circ}C$.

(3) High temperature thermostatic bath. Manufactured at Senno Seisakusho (Manufacturing Company). The testing apparatus was housed in the bath, and the sample was tested after being kept there for two hours. Some temperature deviations, from opening and closing the door to the thermostatic bath, were unavoidable, but were comparatively unimportant.

(4) Method of experiment. The sample is dried beforehand but, prior to use, it is dried again by being kept in a calcium chloride desiccator for 24 hours. Place about 0.05 g of sand in the copper cup, then put about 0.02 g of the sample on it, and then cover it with 0.035 g of sand so that the sample is sandwiched between the layers of sand. Plant the steel pellet in the sand, and drop the falling weight on it to see if the sample explodes. In my experiments, 40 shots of each sample were struck at the same temperature to obtain the heights of fall above and below the critical height (at this height, 20 shots exploded; in other words, at this height, the rate of explosion is 50 percent). The critical height was calculated by the interpolation method.

2. Results of the Experiment

I will omit the obtained measurements, but show the critical heights calculated from them.

(1) White mercury fulminate (weight of the falling weight, 28.15 g).

Test temperature (°C)	50	30	40	-2	-10	-21	-29	-40
Critical height (cm)	15.4	19.4	20.5	23.4	23.4	23.6	23.9	24.4

(2) Crude mercury fulminate (weight of the falling weight, 28.15 g).

Test temperature (°C)	50	40	30	-1	-10	-21	-28	-40
Critical height (cm)	15.7	16.5	17.5	18.6	19.5	19.9	20.6	21.0

(3) Powder mercury fulminate (weight of the falling weight, 28.15 g).

Test temperature (°C)	50	40	30	0	-11	-17	-29	-40
Critical height (cm)	15.4	16.4	17.2	22.4	23.2	23.2	23.9	24.6

(4) Crystalline lead trinitroresorcinol (weight of the falling weight, 16.27 g).

Test temperature ($^{\circ}$C)	50	40	30	-1	-11	-21	-30	-41
Critical height (cm)	6.9	7.7	7.6	10.1	11.3	11.9	12.1	12.7

3. Study of the Results

In the low temperature range, the relationships between the sensitivities of the three types of mercury fulminates and lead trinitroresorcinol and temperatures are roughly expressed in straight lines. Thus, we can say that, of the two theoretical formulas expressing the changes of sensitivity with temperature, Arami's has more universal validity over a wider range of temperature than Taylor's. However, the deviation from the straight line due to the excessive influence of high temperature occurs at a temperature far lower than that indicated by Arami.

In the high temperature range, the heights of fall for crude mercury fulminate roughly fall on the extension of the straight line in the low temperature range, but those of powder and white mercury fulminates fall far below the lines (ref. 27). This phenomenon has much semblance to the phenomenon where, in the pyrolytic reaction of mercury fulminate, the quiescent period of pyrolysis shortens as mercury fulminate changes from rough granules to fine powder. Therefore, the more susceptible the form of mercury fulminate is to heat, the more susceptible its sensitivity is to temperature.

Throughout the whole temperature range, the heights of fall for lead trinitroresorcinol fall roughly on a straight line. It is assumed,

• Lead trinitroresorcinol
x Crude mercury fulminate
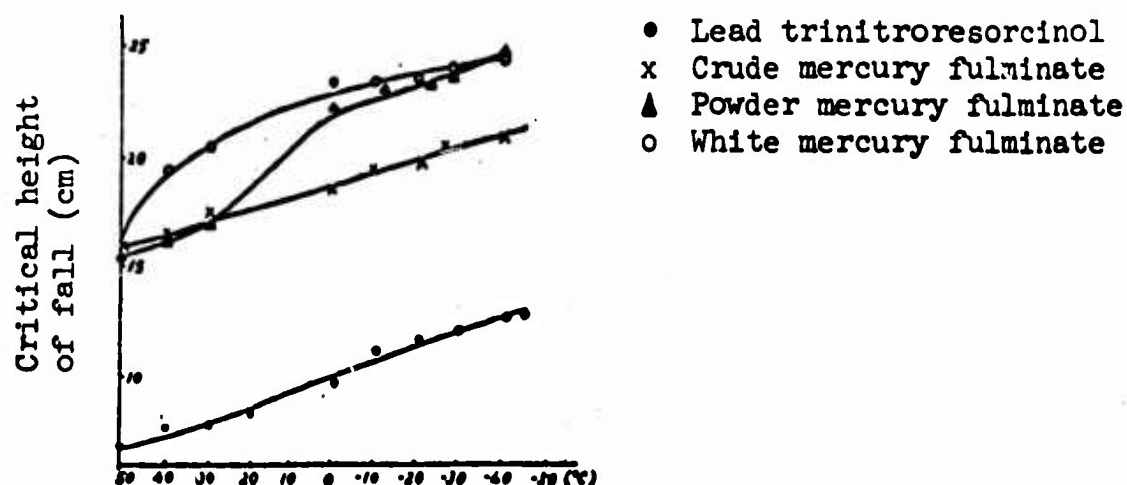▲ Powder mercury fulminate
o White mercury fulminate

Figure 1. Change in sensitivity of initial explosives with temperature.

therefore, that initial explosives like this, with high ignition points, generally have great stability against heat, and that they are affected by heat in a regular way even in the high temperature range.

IV. THE THERMAL SENSITIVITY AND ACTIVATION ENERGY OF INITIAL EXPLOSIVES

1. Equipment and Method of Experiment

(1) Experiment apparatus: A metal bath of Wood's alloy was installed in a vertical electric furnace. Initially, a high temperature control device was used for the purpose of temperature control. It worked normally within the high temperature range between approximately $200°$ and $400°C$, but it was accompanied by an inertia of from $2°$ to $3°C$ per minute. Finally, we ascertained that better results are obtained by skillfully controlling the accessory transformer. The accuracy in this case is $0.5°C$ per minute.

(2) Method of experiment: Insert a glass test tube, length, 80 mm; diameter, 12 mm, into the metal bath, and leave it there for about two minutes. When the glass wall is heated up to the same temperature as the metal bath, take about 0.02 g of sample in a teaspoon and put it in the test tube. You will soon hear an explosion. With a chronograph measure the time between the addition of the sample and the resultant explosion. This is called the time lag of ignition. Make 6 to 18 measurements of this time lag for each initiator within the appropriate temperature range.

2. Results of the Experiment

From the time lag of ignition, obtained in the manner described for each initiator at each appropriate temperature, its activation energy is obtained by means of the following formula (ref. 28),

$$\text{Log } \tau = E/4.574 \ T + C$$

τ: Time lag of ignition in terms of seconds
E: Activation energy
T: Absolute temperature

E as calculated from the above formula and the temperature at which the time lag of ignition is exactly 4 seconds, the so-called ignition point, are summarized and shown below.

Initiator :	Ignition point (^{o}C)	Activation energy (kcal/mol)
Tetracene	147	32
Diazodinitrophenol	164	55
Powder mercury fulminate	205	31
Crude mercury fulminate	208	35
White mercury fulminate	221	30
Lead picrate	263	48
Silver acetylide	267	37
Crystalline lead trinitroresorcinol	295	59
Powder lead trinitroresorcinol	299	57
Anhydrous lead trinitroresorcinol	300	59
Lead azide	318	55
Silver azide	351	41

3. Study of the Results

Under Patry's classification method, initial explosives are classified in the following two categories according to their ignition points and activation energy.

(1) Mercury fulminate type: Tetracene, diazodinitrophenol.

(2) Lead azide type: Silver azide, lead trinitroresorcinol.

Lead picrate or silver acetylide cannot be classified in any of these two categories by the two values alone.

The mercury fulminate type initiators have low ignition points and low activation energy, while the lead azide type initiators have high ignition points and high activation energy.

As Garner and Gomm maintained in their study (ref. 30) of the pyrolysis of lead azide, the simultaneous decomposition of 2 or 3 molecules is an essential condition for triggering a fulminating explosion, and a great deal of activation energy is doubtlessly required for the simultaneous decomposition. On the other hand, such a great amount of activation energy is not required for actuating a combustion of mercury fulminate or the like, because such an actuation is a single molecule reaction.

In the foregoing, I have discussed the characteristics of the mercury fulminate type and the lead azide type initiators by combining the results of Patry's experiment and the information I obtained about their activation energy.

V. IGNITION SENSITIVITY OF INITIAL EXPLOSIVES BY MEANS OF ELECTRIC BRIDGE CURRENT

1. Equipment and Method of Experiment

(1) Experiment apparatus: The principle of leverage is utilized in this apparatus. When the initiator is ignited by the incandescent electric bridge, its explosion pressure blows up the pressure bearing plate placed over it. This automatically breaks the current at the breaking point installed on the other side of the fulcrum (fig. 2). The time between the beginning of the flow of electric current through the bridge and the breaking of the current at the breaking point by the ignition of the initiator is measured by an electric magnetic oscillograph.

The electric wires used for the bridge are made of platinum iridium (platinum, 90 percent; iridium, 10 percent). Diameter, 0.0305 mm; filament resistance, 340 ohm/m (room temperature, 20°C).

The initiator is mixed with about the same amount of a 3 percent gelatin-water solution and kneaded well. Then it is painted on the metal piece holding the bridge so that the bridge is well covered with the paste. Then the painted bridge is kept in a vacuum drier at 50°C for about 10 hours.

(2) Method of experiment. (See figure 2.) First, pull down /147 switch S_2 to the right and measure the resistance of the bridge with the

Wheatstone bridge. Next, pull down switch S_2 to the left and equalize

KEY:
1 - Automatic key
2 - Ele.-mag. oscillograph
3 - High speed switch
4 - Pressure bearing plate
5 - Breaker
6 - Fulcrum
7 - Bridge
8 - 12 V (for breaker)
9 - 6 V (for ignition)
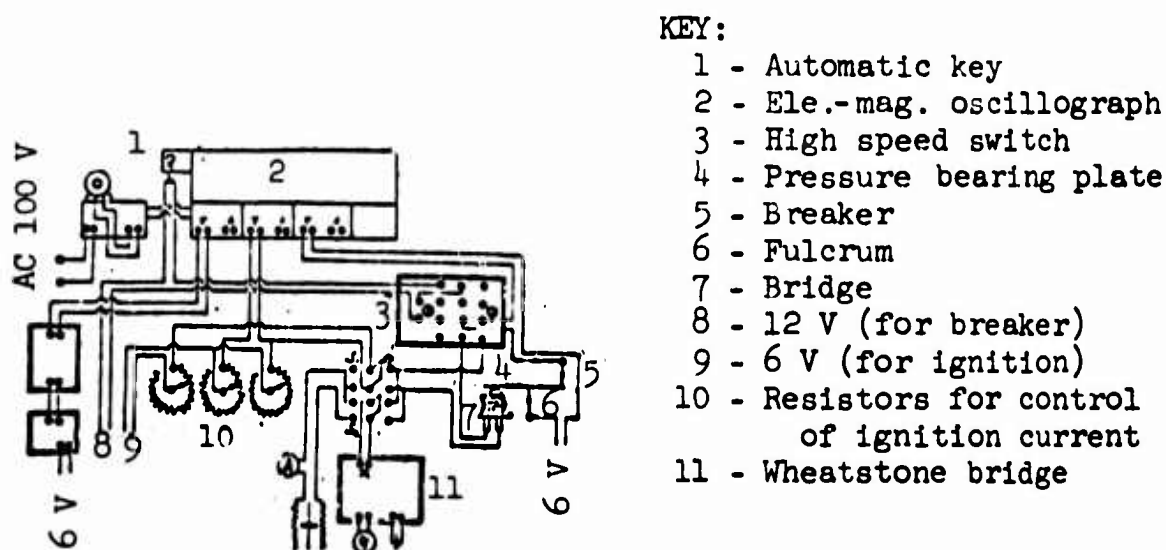10 - Resistors for control of ignition current
11 - Wheatstone bridge

Figure 2

the load resistance to the bridge resistance. Then, push up S_2 and pull down S_1 to the left, and adjust the ignition current to the proper amperage using the ignition current control resistors (three 5-ohm resistors), while controlling the deflection of the oscillograph properly. Then, pull down S_1 to the right, operate the high speed switch using the automatic key, and obtain the oscillograms of ignition current and ignition time.

The pressure bearing plate is supported at the fulcrum and the breaking point, with the center of gravity being slightly to the left of the fulcrum, and the contact maintained at the breaking point. Upon receiving the explosion pressure subsequent to the ignition of the initiator, the plate breaks the current at the breaking point. The time between the beginning of the flow of the ignition current and its breaking at the breaker is measured.

2. Results of the Experiment

(1) Bridge current and ignition time. Bridges were measured with a micrometer, and only those that met the specification of 1 ± 0.05 mm in length were used.

(a) Crude mercury fulminate

I	2.0	1.6	1.3	1.0	0.8	0.7	
S	6.3	8.6	11.6	20.1	37.8		2/5 ignition
I^2S	25.2	22.0	19.6	20.1	23.8		

Notes: I: Ignition current (ampere)
S: Ignition time (1/1000 sec)
I^2S: (Ignition current)$^2 \cdot$ (ignition time)
S values are mean values of 5 measurements respectively.

(b) Powder mercury fulminate

I	2.0	1.6	1.3	1.0	0.8	0.7	
S	2.8	4.0	6.1	10.5	18.7		2/5 ignition
I^2S	11.2	10.2	10.3	10.5	12.0		

(c) White mercury fulminate

I	2.0	1.6	1.3	1.0	0.8	0.6	
S	2.9	3.7	5.2	7.2	15.4		2/5 ignition
I^2S	11.6	9.5	8.8	7.2	9.9		

(d) Crystalline lead trinitroresorcinol

I	2.0	1.6	1.3	1.0	0.8	0.75	
S.	1.4	2.1	3.4	6.4	20.6		3/5 ignition
I²S	5.6	5.4	5.7	6.4	13.2		

(e) Powder lead trinitroresorcinol

I	2.0	1.6	1.3	1.0	0.8	0.75	
S	1.6	2.6	3.9	6.9	26.3		2/5 ignition
I²S	7.2	6.7	6.6	6.9	16.8		

(f) Anhydrous lead trinitroresorcinol

I	2.0	1.6	1.3	1.0	0.8	0.75	
S	1.7	2.7	4.0	8.3	22.0		2/5 ignition
I²S	6.8	6.9	6.8	8.3	14.1		

(g) Lead picrate

I	2.0	1.6	1.3	1.0	0.8	0.6
S	4.3	5.6	6.1	9.1	11.0	31.6
I²S	17.2	14.4	10.5	9.1	7.0	11.4

(h) Lead azide

I	2.0	1.6	1.3	1.0	0.8	
S	2.1	4.0	6.5	13.1		2/5 ignition
I²S	8.4	10.2	11.0	13.1		

(i) Silver acetylide

I	2.0	1.6	1.0	0.8	0.7	
S	4.7	6.5	11.3	29.6		4/5 ignition
I²S	18.8	16.6	11.3	18.9		

(j) Tetracene

I	2.0	1.6	1.3	1.0	0.8	0.5	
S	2.4	3.1	4.1	5.3	6.6		3/5 ignition
I²S	9.6	7.9	6.9	5.3	4.2		
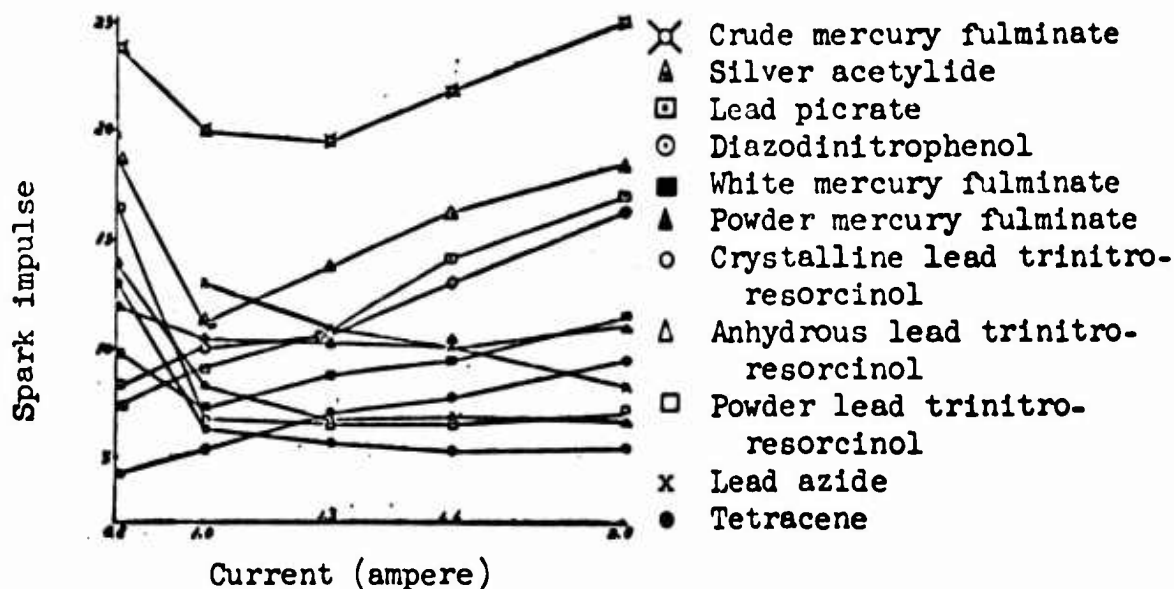
Figure 3. Current-spark impulse curves.

(k) Diazodinitrophenol

I	2.0	1.6	1.3	1.0	0.8	0.6
S	4.1	5.1	6.3	10.1	12.8	
I²S	16.4	13.1	10.7	10.1	8.2	

1/5 ignition

From these measurements, the relationships between spark impulses and ignition current amperages are plotted into curves as shown in figure 3.

(2) Bridge length and ignition time. Three lengths (1, 2 and 3 mm) of platinum iridium wire bridges were used. These three kinds of bridges were painted with white mercury fulminate, and a fixed quantity of electric current was passed through them to measure the ignition times. The reason why white mercury fulminate was chosen for the test is that its purity is high, and its granules are perfectly crystalline and uniform in size, and therefore the variance of results is expected to be smaller than in the case of other initial explosives.

(a) When the bridge is 1 mm long

R	0.55	0.57	0.55	0.53	0.47	0.52	0.50
I	2.0	1.6	1.3	1.0	0.8	0.7	0.6
S	3.7	4.5	5.2	7.3	15.8	29.0	

2/5 ignition

Note: R: Electric resistance (ohm)

(b) When the bridge is 2 mm long

R 0.93 0.81 0.83 -0.96 0.78 1.01 0.81

I 2.0 1.0 1.3 1.0 0.8 0.7 0.4

S 2.8 4.2 4.9 7.2 12.1 i3.3   2/5 ignition

(c) When the bridge is 3 mm long

R 1.30 1.38 1.28 1.26 1.44 1.52 i.31

I 2.0 1.6 1.3 1.0 0.8 0.7 0.4

S 2.1 3.7 4.4 6.1 9.4 14.0   4/5 ignition

In order to facilitate the examination of the above results, tests were conducted without any initiator painted on the bridges. That is, the bridges themselves were electrified, and the electric current intensified until the bridges were burned out. The intensity of the current at the time of the burning out is measured and recorded as the burning-out current.

	Length of bridge (mm)	Resistance (ohm)	Burn-out current (A)
Average	1.00	0.432	0.940
Maximum	1.13	0.565	1.110
Minimum	0.82	0.365	0.750
Average	1.99	0.747	0.622
Maximum	2.32	0.864	0.708
Minimum	1.69	0.612	0.550
Average	3.04	1.100	0.534
Maximum	3.41	1.281	0.572
Minimum	2.49	0.869	0.510

Note: The length average is that of 10 lengths.

3. Study of the Results

K. Drekopf (ref. 31) studied the phenomenon of bridge type electric detonators. He examined the phenomenon of temperature rise of electrified bridges and came up with a general theoretical formula. According to the formula, the temperature rise at the surface of the bridge, namely that surface in direct contact with the painted initiator, is, if we assume there is no loss of heat by conduction, in proportion to the product of the second power (square) of the electric current and the current time, namely the spark impulse. On the other hand, it is in

inverse proportion to the square of the section area of the bridge, namely the fourth power of the bridge's diameter. In other words, Drekopf's formula applies accurately in case the bridge is infinitely long and there is no loss of heat at the ends.

However, for practical purposes, since the lengths of bridges are 1 - 3 mm, we must consider a considerable loss of heat to occur at the ends. If we take these conditions into account, the theoretical handling of the phenomenon becomes extremely complicated.

The foregoing considerations lead us to the conclusion that Drekopf's formula is significant only in a qualitative way, and that for practical quantitative data we must still rely on actual experiment. In this sense, the measurements that I obtained are significant.

The relationship between the bridge current and the ignition time shows a relatively regular curve.

Further, it was found out that initial explosives can be classified into the following three categories according to the relationships between spark impulses and ignition currents.

(1) Spark impulse decreases as ignition current decreases: Crude mercury fulminate, white mercury fulminate, lead picrate, silver acetylide, tetracene, diazodinitrophenol.

(2) Spark impulse remains about the same irrespective of ignition current: Powder mercury fulminate, crystalline-, powder-, and anhydrous-lead trinitroresorcinols.

(3) Spark impulse increases as ignition current decreases: Lead azide.

A review of the results of this classification reveals that those falling under category (3) correspond to the lead azide type initiators under Patry's classification, and those belonging to category (1) correspond to the mercury fulminate type. In the cases of lead azide and the like, where a simultaneous decomposition of 2 or 3 molecules is required, it is more effective to turn on a relatively large quantity of electricity for an extremely short time than to charge with a small amount of electricity for a relatively long time. In other words, a fulminating explosion cannot readily be triggered by giving for a long time some energy that is inadequate for causing a simultaneous decomposition of several molecules, but a fulminating explosion can easily be actuated by giving adequate energy for a short time. However, in cases of mercury fulminate type initiators, where only a small amount of energy is required to cause a single molecular decomposition, it is sufficient to run a small quantity of electricity for a short time.

As a result of obtaining the spark impulses of various initial explosives, we have produced a new fact endorsing Patry's line of reasoning that the explosive pyrolysis, namely the fulminating explosion, of lead azide type initiators is triggered by a simultaneous decomposition of several molecules, and that the explosive pyrolysis, namely the combustion, of mercury fulminate type initiators is brought about by a single molecular decomposition.

Of the initiators belonging to category (2), powder mercury fulminate has a smaller grain size than the other mercury fulminates, and therefore adheres to the bridge much better. For this reason, the thermal conduction from the surface of the electrode is more effective. Thus, powder mercury fulminate has lost most of the characteristics that the other forms of mercury fulminate have with regard to the spark impulse and ignition current. The grain size of crude mercury fulminate, on the other hand, is too great to be used properly on the bridge. In this case, the loss of heat by radiation from the surface of the bridge is considerable. These facts have great practical usefulness.

As to the properties of lead trinitroresorcinol, it is extremely interesting to examine these from the viewpoint of molecular structure. I will discuss this aspect at the end of this report.

As a result of the measurement of the relationship between the length of the bridge and the ignition time, it was learned, as far as the bridges of 1 – 3 mm lengths are concerned, that the loss of heat increases remarkably as the length of the bridge decreases.

The values of burning-out current in the case of unpainted bridges, and those of ignition time in the case of bridges painted with white mercury fulminate, increase as the bridges are shortened. This trend magnifies as the current diminishes.

The product of the spark impulse times the bridge resistance indicates the quantity of heat required for ignition. Therefore, by maintaining a constant value of the bridge resistance, we can use the spark impulses as the relative values of the quantities of heat required for ignition.

The foregoing thermal properties are summarized below.

Initiator	Spark impulse (I^2S)	Instant ignition point ($^{\circ}C$)	Activation energy (kcal/mol)
Crude mercury fulminate	20.1	206	35
Lead azide	13.1	318	55
Silver acetylide	11.3	267	37

(contd)

(table continued from preceding page)

Initiator	Spark impulse (I^2S)	Instant ignition point (^{o}C)	Activation energy (kcal/mol)
Powder mercury fulminate	10.5	206	31
Lead picrate	9.1	283	48
Diazodinitrophenol	8.9	164	55
Anhydrous lead trinitro-resorcinol	8.3	300	59
White mercury fulminate	7.2	221	30
Powder lead trinitro-resorcinol	6.9	299	57
Crystalline lead trinitro-resorcinol	6.4	295	59
Tetracene	5.3	147	32

Note: Spark impulses listed above are at 1 A current.

From the above table, I discovered a unique property of lead tri-nitroresorcinol as it is ignited by a bridge; i.e., from its ignition point and activation energy, it is naturally presumed that its spark impulse also would be about the same as that of lead azide. However, its spark impulse is far smaller, and is about equal to that of tetracene.

In an effort to find the reason for this peculiarity, we compared lead trinitroresorcinol with lead picrate, which has a similar molecular formula.

The following values are taken as the interatomic distances in the molecule[1]

$$C - C = 1.39 \qquad C - N = 1.47 \qquad C - O = 1.45$$
$$O - Pb = 1.47 \qquad N - O = 1.21$$

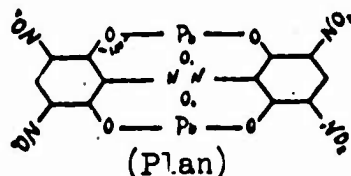$$O, \text{ valence angle} = 110^{o} \quad N\angle{}_{O}^{O} \quad \theta = 127^{o}$$
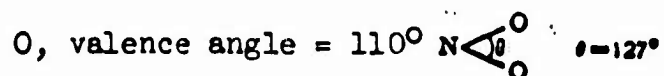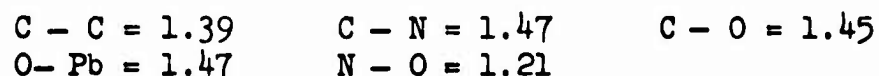
From these values, the following molecular structure is considered to be most resonable

(Plan)
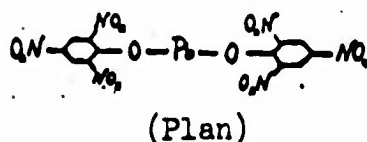
[1]Interatomic distances are all taken from L. Pauling (ref. 32).

(Elevation)

Similarly, let us consider molecular structures for lead trinitro-resorcinol. First, we take the following as a cyclic molecular structure.

(Plan)

But the valency angle of oxygen becomes 120°, which is too great. Furthermore, the nitro groups contained in the ring formed by Pb, O and C are excessively close together. Therefore, it is appropriate to give up such an unstable cyclic structure.

Let us consider next straight chain structures.

I   (Plan)

(Elevation)

(Plan)

II

(Elevation)
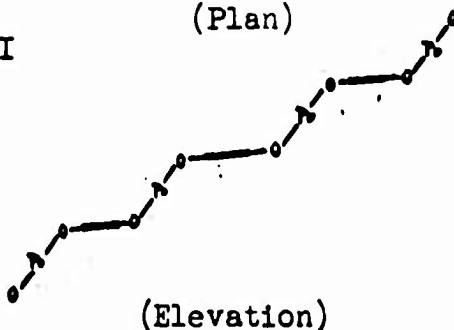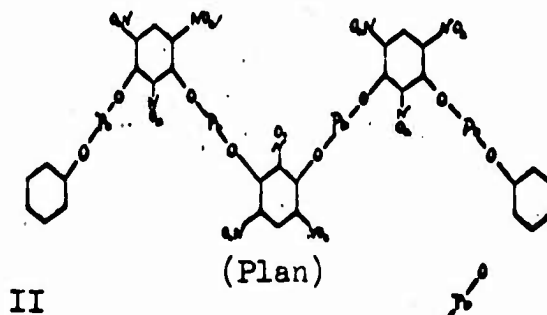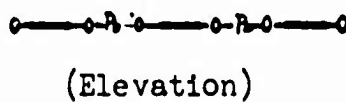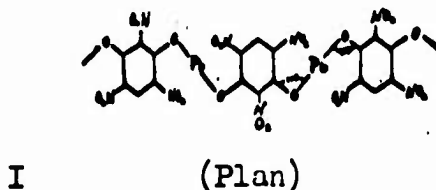
We consider the straight chain molecular structures I and II.
Which of these two is more reasonable can only be determined by experiment. In any event, the straight chain form is more reasonable than the cyclic form.

The properties of the two lead salts are compared below.

	Impact sensitivity (cm)	Spark impulse (I^2S)	Instant ignition point (^{o}C)	Activation energy (kcal/mol)
Lead picrate	30 or more	9.1	283	48
Lead trinitro-resorcinol (crystalline)	2	6.4	295	59

Note: The impact sensitivity was obtained by the silver sand test. The values show the heights of fall (maximum) at which explosions do not occur. (Falling weight, 16.27 g)

In such cases as the measurement of ignition points when heat comes from all around, a long straight chain structure molecule similar to that of lead trinitroresorcinol is swung into a molecular vibration by the energy thus given. Since it absorbs energy uniformly, it can stay stable even when a relatively large amount of energy is given. However, a short molecular structure such as that of lead picrate vibrates violently when given a large amount of energy in the manner described, and it decomposes following such a vibration much sooner than the former.

In other cases as the ignition of initiator by means of an incandescent bridge, where a concentrated heat energy is given locally and instantaneously, the situation develops quite differently than when heat was given gradually and peripherally. A short structure molecule can absorb the given energy, and immediately swing into a uniform molecular vibration. However, a long straight chain structure molecule cannot remain so composed, but will have a violent local interatomic vibration, which finally breaks and destroys the molecule. Under this reasoning, we can understand the reason for the strikingly small spark impulse of lead trinitroresorcinol.

The method of giving mechanical energy in the falling weight impact test resembles that employed in the ignition of explosives by means of an incandescent bridge; i.e., in both cases, an outside energy is given locally and instantaneously. Thus, one of the reasons why lead trinitroresorcinol shows a remarkably greater sensitivity to impact than

lead picrate is explained by the aforementioned difference in molecular structure.

VI. THE IMPACT SENSITIVITY OF INITIAL EXPLOSIVES AND THE SECONDARY STRUCTURE OF THEIR CRYSTALS

1. Differences in Impact Sensitivity Among Various Forms of Mercury Fulminate

It is empirically well known about initial explosives in general that, the greater their crystal grain sizes are, the greater their impact sensitivity within a certain range. However, as to the reasons, explanations are not convincing. It has been merely assumed that, as the crystal size increases, the intramolecular strains of molecules composing the crystal intensify.

I assumed that the secondary structure (ref. 33) of crystal must be an important factor affecting the sensitivity of an initiator, and set about proving my assumption. The existence of the secondary structure of crystal has recently been confirmed by X-ray studies, and proved quite instrumental in explaining mechanical strengths and breaking phenomena of various substances.

In Chapter III, the results showed that each of the three forms of mercury fulminate, crude, powder and white, have different impact sensitivity. Crude mercury fulminate comes mostly in diamond-shaped plate crystals, whose sizes are approximately $0.089 - 0.173$ mm. The granules of powder mercury fulminate are extremely irregular and jagged balls, whose sizes are approximately 0.046 mm or smaller. White mercury fulminate forms perfect octahedron crystals, whose grain sizes are approximately 0.074 mm or smaller. (The observation of the grain sizes of the three types of mercury fulminate was conducted microscopically and by means of plane X-ray photographs taken by the Debye-Scherrer method.)

The interatomic distances as obtained from the X-ray photographs. are shown in the following table.

From the values indicated in the table, we learn that among the three forms, there is no difference in the basic structure of crystal. Therefore, it is realized that the difference in sensitivity does not result from the basic structure itself. The purpose of my comparing between the crude form and the powder form was to see if there is any such phenomenon as the strain of crystal due to an external force, as this phenomenon is often observed in cases of metals.

Mercury fulminate

White		Crude		Powder	
Strength	Interlattice-plane distance, Å	Strength	Interlattice-plane distance, Å	Strength	Interlattice-plane distance, Å
10	0.99	10	0.99	10	0.99
5	1.02	5	1.02	5	1.02
10	1.02	10	1.03	10	1.03
2	1.04	3	1.04	3	1.04
2	1.05	3	1.06	3.	1.05
7	1.07	7	1.07	7	1.07
4	1.08	4	1.09	4	1.08
4	1.11	4	1.11	4	1.11
2	1.14	5	1.14	5.	1.14
2	1.16	4	1.15	4	1.16
4	1.20	5	1.21	5	1.20
4	1.24	6	1.26	6	1.24
6	1.28	4	1.28	4	1.27
6	1.34	4	1.33	4	1.33
4	1.39	6	1.38	6	1.39
2	1.50	4	1.50	4	1.50

According to Taylor's tritochemical theory as referred to in Chapter I, powder mercury fulminate, with an extremely larger surface area, should show a greater sensitivity than crude mercury fulminate, whose grain size is larger and surface area smaller. However, the results of the experiment indicate a reverse situation.

Furthermore, white mercury fulminate, whose purity is higher than that of the other two, shows less sensitivity.

2. Grain Size and Impact Sensitivity of Lead Trinitroresorcinol

Grain size (sieve mesh)	Height of fall (cm)	No. of explosions (per 40 shots)	Critical height of fall (cm)	Instant ignition point (°C)
300 or more	13 11	22 16	12.0	298
300-200	11 9	23 19	9.5	295
200-150	15 12	23 15	13.8	297
150-80	15 12	22 16	14.0	298
80 or less	20 17	21 18	18.9	298

Using such grain sizes as shown in the above table of lead trinitroresorcinol as samples, we conducted silver sand tests at room temperature in order to obtain the critical heights of fall (weight of falling weight, 16.27 g). Further, their instantaneous ignition points were measured in the manner described in Chapter IV.

The above table shows that the instantaneous ignition point remains about the same irrespective of the grain size, but that the impact sensitivity is influenced remarkably by this grain size.

3. Existence of Irregular Spots (defects) and the Secondary Structure of the Crystal of Mercury Fulminate

I came to consider that the concept of the secondary structure of crystal in the solid state theory should be introduced in order to give an adequate explanation of the results of the experiment with mercury fulminate and lead trinitroresorcinol.

I tried to prove the existence of the so-called irregular spots (Loecherstellen) and the so-called secondary structure (or mosaic structure) in the crystal of mercury fulminate.

(1) Microscopic observation of the crystal of mercury fulminate: An observation of the 400 times magnified photographs of single crystals

of crude and white mercury fulminates revealed that neither of them was a perfect crystal, and that the former showed venous streaks and the latter concentric rings.

(2) Microscopic observation of the change in a single crystal of white mercury fulminate when heated: Before being heated, it has the appearance of a white transparent diamond-shaped plate crystal. After 30 minutes of heating at $100^{\circ}C$, the crystal turns light yellow, yellow spots develop on the surface and in various parts of the interior, and straight cracks develop parallel with the longer axis of the crystal. After 60 minutes of heating, the yellowish color deepens, the yellow spots spread in size and increase in number, and the cracks increase and cause part of the crystal to chip off. After 90 minutes of heating, the crystal is tinted brown, and the straight cracks increase still further. After 120 minutes, the entire crystal turns brown. After 150 minutes of heating, it turns dark brown and many tiny fragments develop. Its explosive property is lost already.

(3) X-ray observation of the change in crystals of crude mercury fulminate when heated: A small amount of crude mercury fulminate is pasted thinly over a piece of thin sheet glass. While heating this sample at $100^{\circ}C$, plane X-ray photographs are taken according to the Debye-Scherrer method. Before heating, the diffraction point is clear. After 4 hours, the external appearance remains the same, but somewhat yellow brown. The diffraction point by X-rays begins to drag a long tail. After 8 hours, the entire sample turns brown, but the shape of the crystals remains unchanged. The diffraction point now has a still longer tail and the intensity of the point is weakened. After 12 hours, the entire sample turns dark brown, but the crystals remain almost unchanged in shape. The diffraction point becomes more vague.

These phenomena are interpreted as follows. The crystal of mercury fulminate gradually decays toward the secondary structure, while the arrangement of microcrystals becomes utterly irregular, so that finally the X-rays are reflected in all directions and cannot form any spot at all. However, an observation of the external appearance after 12 hours of heating can hardly detect any change from before heating. Yet, this substance, if heated rapidly, burns in a violent combustion but does not explode. Therefore, it is considered that the disappearance of the spot is not due to the complete degeneration of mercury fulminate, but that it is due primarily to the decay toward the secondary structure.

(4) Observation of the explosion of a single crystal of white mercury fulminate by instantaneous heating: A single crystal of white mercury fulminate is placed on a sheet of glass and heated rapidly with a gas flame. It explodes instantaneously. An examination of the traces reveals the following. First, the crystal breaks down into a number of

fragments that scatter in all directions. Then, each of these fragments in turn explodes and scatters finer particles; i.e., the given heat runs through the irregular spots, causing pyrolysis in these spots and breaking the crystal into fine fragments. These fine fragments in turn explode under a tremendous amount of heat.

(5) Microscopic observation and X-ray observation of the collapse of crude mercury fulminate crystals due to pressure filling into a detonator: Crude mercury fulminate is pressure-filled into copper cups

under 100, 500, 1000 and 3000 kg/cm^2 pressures, respectively. Then, magnified photographs are taken of the surface areas of the mercury fulminate in these detonators. The detonators in turn are soaked in water, and the mercury fulminate is scooped out. Another series of magnified photographs are taken of the mercury fulminate in loose form. Finally, plane X-ray photographs are taken of the powder by the Debye-Scherrer method.

The plane X-ray photographs show rings mixed with spots in the

powder under a 100 kg/cm^2 pressure, and rings only under 500 kg/cm^2 or

greater. The fulminate under a 3000 kg/cm^2 pressure shows weak rings. The rings are brought about by the fact that large crystals crumble under the compression, diffracting the X-rays just the way a mass of

powder does. Under a strong 3000 kg/cm^2 pressure, the fulminate crumbles down to the secondary structure, making the arrangement of micro-crystals irregular and diffusing the diffracted X-rays.

4. Explanation of Changes in Impact Sensitivity with Grain
    Size from the Viewpoint of the Secondary Structure

The various phenomena I have described heretofore convince us beyond any doubt that irregular spots or defects exist in the crystals of lead trinitroresorcinol as well as mercury fulminate of various forms used in the sensitivity test. Therefore, the possibility of the energy of an external force concentrating on the irregular spots of the crystal is greater with the crude form and the powder form of mercury fulminate than with the highly pure white form. Further, the reason why the crude form is more sensitive than the powder form is that the internal defects constitute a more influential factor than the external defects.

The curve showing the relationship between the grain size and sensitivity of lead trinitroresorcinol has a minimum point. This means that when the crystal size is too great in relation to the weight of the falling weight, most of the energy is consumed in breaking the crystals

down, and the probability of the surplus energy flowing along the cracks and triggering the explosion becomes small. In order to confirm this reasoning, it will be necessary to conduct sensitivity tests on the same sample using heavier falling weights.

VII. ANALYSIS OF THE CRYSTAL STRUCTURE OF MERCURY FULMINATE

1. Determination of the Space Group by Means of
   an X-ray Goniometer

For the purpose of the analysis of crystal structure, I was allowed to use the Weissenberg X-ray goniometer and the Bragg ionization spectrometer belonging to the Mineralogical Laboratory, Science Department, Tokyo University.

The same sample as described in Chapter II was used for the analysis. The dimensions of the unit cell are as follows (ref. 34)

$$a = 7.71\text{Å} \qquad b = 5.48\text{Å} \qquad c = 10.43\text{Å}$$

This unit cell contains 4 molecules.

Now, let us determine the space group. The results of examination of lattice points as appearing in the X-ray photographs are consolidated as follows.

(hkl)	$(hk0)$	$(0kl)$	$(h0l)$
111	020	020	200
211	200	002	202
113	220	022	400
311	040	040	402
131	400	042	600
151	420	004	102
511	440	024	204
115	240	006	206
117	600	026	006
331	-	008	008.
313	-	041	-
133	-	-	-
351	-	-	-
513	-	-	-
153	-	-	-
222	-	-	-
232	-	-	-
224	-	-	-
243	-	-	-

From these, the following properties of superstructure are obtained

(i) hkl $h+k+l=n$
(ii) $hk0$ $h=2n$
(iii) $0kl$ $k=2n$
(iv) $h0l$ $l=2n$

From the foregoing, it is appropriate to regard the space groups as D_{2h}^{15}. The following coordinates are obtained for the 4 atoms of mercury and 8 atoms of oxygen, nitrogen and carbon (ref. 35)

$4(Hg): 000; \frac{1}{2}\frac{1}{2}0; 0\frac{1}{2}\frac{1}{2}; \frac{1}{2}0\frac{1}{2}$

$8 \begin{cases} (O) \\ (N) \\ (C) \end{cases}$ $xyz; \frac{1}{2}+z\ \frac{1}{2}-y\ \bar{z}; \bar{z}\bar{y}\bar{z}.$
$\frac{1}{2}-z\ \frac{1}{2}+yz; \bar{z}\ \frac{1}{2}+y\ \frac{1}{2}-z; \frac{1}{2}-zy\frac{1}{2}+z$
$z\ \frac{1}{2}-y\ \frac{1}{2}+z; \frac{1}{2}+z\ y\ \frac{1}{2}-z$

Structure factors

$$A = 8\cos 2\pi[h(z-\tfrac{1}{4})+k/4]\cos 2\pi[k(y-\tfrac{1}{4})+l/4]$$
$$\cos 2\pi[l(z-\tfrac{1}{4})+h/4]$$
$$B = 0$$

In the above space lattice, mercury forms a face-centered cubic lattice. The reflecting power of mercury is so strong that it dominates the degree of reflection at each lattice point. Therefore, at such lattice points where mercury atoms cancel each other, atomic groups like the fulminic group whose reflecting power is extremely weak, but not the mercury atoms, participate in the reflection. Necessarily, this reflection is very weak in intensity. From among the aforelisted lattice points, those at which the mercury atoms cancel each other's reflecting power are chosen below and their intensity of reflection is studied.

(102)   Weakest
(211)   Weak
(041)   Weakest

These results are exactly those expected. This proves that the space group determined above was right.

2. I will omit the various calculations involved in the measurement of the integrated reflection by the ionization spectrometer. I will show below what I obtained by calculation of structure factors, what

I obtained from actual measurements and what I arrived at after making various corrections. These values agree with one another relatively well as seen below.

(ool)	F(calculated)	F(measured)	F(corrected)
002	281	192	286
004	237	162	237
006	215	147	196
008	165	113	168
0010	411	78	147
0012	101	69	126
0014	75	51	113

Note: Considering the influence of temperature on the screening effect and reflection, I assumed that the measured values are equal to the calculated values when the intensity of reflection is at its mean value, namely $1 = 4$, and multiplied the value of each lattice plane by this coefficient for the purpose of correction.

(oko)	F(calculated)	F(measured)	F(corrected)
020	244	81	185
040	174	52	86
060	136	43	58

Note: I made an allowance for the decrease of the incident X-rays resulting from the angle formed between the crystal and the X-rays. If the area of plane (oko) is S, its section area in the direction of the incident X-rays is S sin θ. The correction was made by the following formula

$$F^2(\text{corrected}) = F^2(\text{measured})\ 1/\sin\theta$$

(hoo)	F(calculated)	F(measured)
200	272	166
400	212	79
600	170	58
800	142	55
1000	120	-

As a result of the foregoing analysis, it appears certain that the mercury atoms in the crystal of mercury fulminate form a face-centered cubic lattice. The next question pertains to what position the fulminic group assumes. In the path to the solution of this question lies exactly the same obstacle as encoutered in the analysis of the crystal structures of mercury oxide (ref. 36) and mercuric chloride (ref. 37). The reflecting power of the mercury atom, being so markedly greater than the reflection of the crystal, is hardly affected by the other lighter atoms bonded with the mercury atom, making the analysis extremely difficult.

3. Quantum-Chemical Considerations of the Molecular Structure of Mercury Fulminate in the Crystal

In order to draw a most rational picture of the crystal by properly positioning the fulminic group in relation to the mercury atoms that form a face-centered cubic lattice, I decided to study the structure by introducing the concept of quantum resonance in the quantum theory to the fulminic group. Since Pauling has clarified the azide ion from the standpoint of the quantum theory, I will base my considerations on his findings.

(1) Quantum resonance in the fulminic ion: This ion has 16 valency electrons just as the azide ion has. It has a straight line type structure of O-N-C with the N atom at the center. For the atoms to oe stable, these valency electrons should be arranged on the L orbit. The following two most probable methods can be considered

$$
\begin{array}{ll}
A & :\ddot{O}-N\!\!=\!\!\ddot{C}\!\!: \\
B & \ddot{\ddot{O}}-N\!\!\equiv\!\!C\!\!: \\
\end{array}
$$
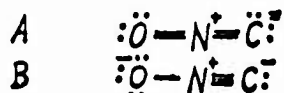
Each of these structures has four covalent bonds (a double bond and a triple bond are counted as 2 and 3, respectively). In each structure, the electric charges are separated between adjacent atoms. Incidentally, other structures than these two can be drawn, but it does not take long to realize that they are far more unstable than the two previously mentioned structures. For example,
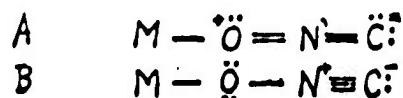
$$
C \quad \ddot{\ddot{C}}-N\!\!\equiv\!\!O\!\!:
$$
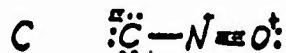
is assumed to be extremely unstable due to its distribution of electric charges. And

$$
\begin{array}{ll}
D & :\ddot{C}=\ddot{N}-\ddot{O}\!\!: \\
E & :\ddot{C}-\ddot{N}\!\!=\!\!\ddot{O}\!\!: \\
\end{array}
$$
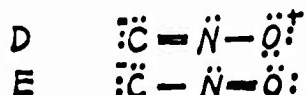
are both unstable because their covalent bonds are too few.

Structures A and B are so much alike in nature that there cannot be any discernible difference in energy between the two. Therefore, it is impossible to determine which of these two structures is really assumed. In addition, these two satisfy other resonance conditions. Namely, they have an equal number of unopposed electrons (in this case, it is 0), and roughly the same balanced nuclear structures (i.e., the tetrahedral atom at the center has either two double bonds, or one single bond and one triple bond, and in either case, the configuration of the nuclei is linear in relation to the central atom). Therefore, it is expected that in the normal condition of the molecule, structures A and B resonate each other. It is further expected that the above-mentioned low stability structures, too, are concerned here in a small way, but their degree of concern is so negligible that we can afford to disregard them in the following study. In this way, the molecule becomes more stable than it would be if its normal condition is to be indicated by either structure A or B alone. The degree of stability is equal to the quantity of resonance energy between the two structures. Also, the interatomic distances and the bonding strength constants are not solely for structure A or B, but for the resonant structure between the two.

(2) Molecular structure of mercury fulminate: If we assume that a fulminate of a heavy metal like mercury resonates between structures A and B, the following forms are considered

$$A \qquad M - \overset{\bullet\bullet}{\overset{\bullet}{O}} = \overset{\bullet}{N} - \overset{\bullet\bullet}{\overset{\bullet}{C}}$$
$$B \qquad M - \overset{\bullet\bullet}{\underset{\bullet\bullet}{O}} - \overset{\bullet}{N} \equiv \overset{\bullet\bullet}{C}$$

Form A violates the rule of adjacent charges, leaving form B alone as the structure, thus denying the existence of a resonant bonding structure. Therefore, I obtained the following interatomic distances between the atoms from their covalent bonding radii.

$$O-N \qquad 0.66\text{Å}+0.70\text{Å}=1.36\text{Å}$$
$$N^+{\equiv}C^- \qquad 0.55\text{Å}+0.60\text{Å}=1.15\text{Å}$$

Note: In the latter formula, the values for uncharged atoms were used, because the interatomic distances cannot be affected by the charges since the atoms carry mutually opposing charges. In other words, under the influence of the charges, the C atom will have an increased atomic radius while the N atom will have a decreased one.

Then, the valency angle of oxygen and the interatomic distance of Hg-O were studied. The valency angle is 110° as in the case of other oxygen compounds (ref. 38). No adequate reference material can be found as to the distance of Hg-O. However, most of the fulminates of heavy metals show the characteristics of the molecular bond as in the case of azides, and only a few show the characteristics of the ionic bond.

Therefore, from the tetrahedral covalent bonding radius (ref. 39), the following value is obtained:

$$\text{Hg-O} \qquad 1.48\text{Å} + 0.66\text{Å} = 2.14\text{Å}$$

The electron concerned in the bonding of mercury is the S-electron, and the two bonding arms fall on a straight line. The bonding arms of mercury are hardly ionic, but mostly molecular, as is confirmed in cases of mercurous and mercuric chlorides (ref. 42).

In conclusion, the most rational molecular structure of mercury fulminate is as follows
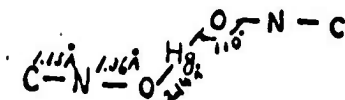
4. Determining the Image of Crystal of Mercury Fulminate

I tried to construct the above-defined molecule most rationally in the unit cell of the face-centered cubic lattice formed by mercury atoms. The lengths of axes of the unit cell are a = 7.71Å, b = 5.48Å,

c = 10.43Å, as described. Therefore, the longest direction of the molecule is brought in line with the longest axis of the cell, namely axis c. Next, the angle formed between the molecular plane and the (010) plane must be determined. In order to allow the existence of such a plane of symmetry as to satisfy the condition of D_{2h}', there is no

choice but assume the angle formed between the molecular plane and the (010) plane to be 0, and the (010) plane to be the plane of symmetry. The (100) and (001) axes are respectively positioned perpendicular to the main axis of rotation, and yet they are axes of rotation perpendicular to each other, positioned in such a way that the plane they form correspond with the plane of symmetry. Further, if the molecules are arranged so as to satisfy the symmetrical working of D_{2h}^{15}, such arrangements as shown in figures 4, 5 and 6 are considered.

From these images of crystal, I obtained by calculation structure factors F and compared them with measured values. The angle formed between the O-Hg-O axis and the (100) axis on the (010) plane is called θ, conveniently. By changing θ, we get different F values. We obtain the value of θ that gives an F value closest to the measured value.
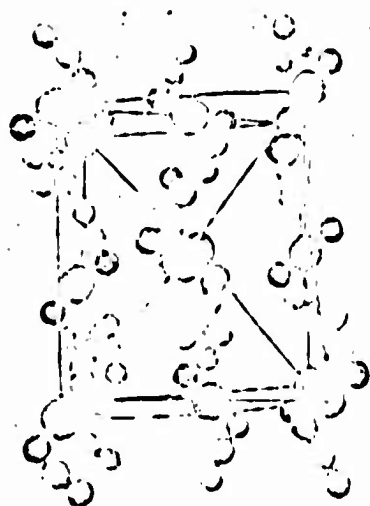
As a result of calculation, the following is revealed.

Figure 4. A model of crystal structure of mercury fulminate. Viewed from the direction of the (010) axis.

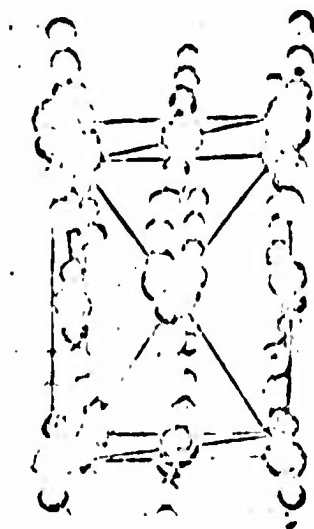Figure 5. A model of crystal structure of mercury fulminate. Viewed from the direction of the (100) axis.

For the F(oko) curve, the relationship between F(080) and F(0100) is,

in the case of $\theta < 30^{\circ}$ F(080) < F(0100).

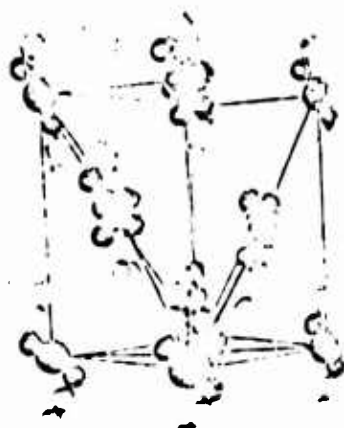This does not agree with the measured values.

Figure 6. A model of crystal structure of
mercury fulminate. Viewed from the direc-
tion of the (110) axis.

For the $F(ool)$ curve, the relationship between $F(006)$ and $F(008)$
is,

in the case of $\theta > 55^{\circ}$ $F(006) < F(008)$.

This is another inversion, and does not agree with the measured value.

Therefore, θ falls between 30° and 55°. This means that the posi-
tioning of molecules as described is not erroneous.

VIII. STUDIES OF THE PROPERTIES AND EXPLOSION MECHANISM OF MERCURY FULMINATE BASED ON THE IMAGE OF ITS CRYSTAL

Based upon the image of the mercury fulminate crystal, various phe-
nomena of the crystal are clarified and its explosion mechanism is
discussed below.

1. Form of the Mercury Fulminate Crystal

The form of fine mercury fulminate crystal is bipyramidal. The
large crystal is of a diamond-shaped plate form. It is easily presumed
that the plane of the plate is parallel with the (010) plane, and that
in the image of crystal obtained previously, the various atomic planes
parallel with the (010) plane are bonded together with weaker Van der
Waals attraction than other planes.[1]

Therefore, it is natural that these atomic planes are most sus-
ceptible to peripheral mechanical disturbances in the process of the

[1]Dr. Yamaguchi of the Institute of Sciences has given an extremely clear
explanation of the relationship between the lattice plane cleavage and
Van der Waals attraction in his study of electron diffraction of cadmium
halides (ref. 41).

growth of crystal. For this reason, it seems quite natural that, in the large crystal, only the (001) and (100) planes grow, making the crystal a plate form. Thus, I could clarify the relationship between the large crystal and the fine crystal that assume remarkably different forms (fig. 7).

Furthermore, X-ray photographs were taken by the Debye-Scherrer method and the following interatomic distances were obtained. The values agree well between the two forms of crystal, endorsing the validity of the foregoing reasoning.

Fine bipyramidal form of white mercury fulminate		Rough diamond-plate form of white mercury fulminate	
Intensity	Interlattice distance	Intensity	Interlattice distance
10	0.99	10	0.99
5	1.02	5	1.02
10	1.02	10	1.03
7	1.07	7	1.07
4	1.08	5	1.08
4	1.11	2	1.11
6	1.28	4	1.28
6	1.34	4	1.32
6	1.36	6	1.36

Note: Those of extremely weak intensity were omitted.

2. Oriented Cracking of the Crystal of Mercury Fulminate

The large plate form crystal of white mercury fulminate easily cracks along the c axis of crystal when given such a mechanical force as
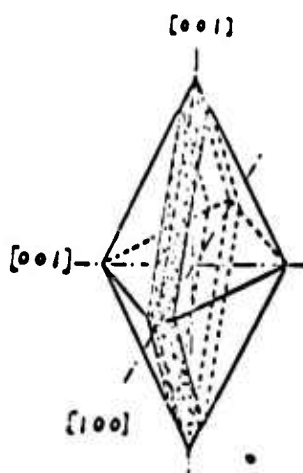

Figure 7

pricking with a needle point, or when given such heat as described in Chapter IV. This phenomenon can be explained as due to the fact that, in the crystal image obtained, the Van der Waals attraction among atoms parallel with the (100) plane is the weakest next only to the (010) plane.

3. Position of Impurities in the Crystal of Crude Mercury Fulminate

Crude mercury fulminate is generally known to be gray in color. This color is due to the mixing of free mercury in the crystals. When dissolved into a sodium thiosulfate solution, crude mercury fulminate turns slightly dark gray. If this solution is filtered, the white filter paper turns slightly gray. When observed microscopically, gray granules of metallic luster will be noticed between the fibers of the paper. This fact has already been reported by L. Woehler (ref. 42).

I examined the crystal image obtained, expecting to place this mercury somewhere in the crystal, and found its place to be among the atoms parallel with the (010) plane and having the weakest Van der Waals attraction. Also, it is considered possible that the atomic mercury occupies one of the lattice points, constituting one type of the irregularities (defects) of the crystal lattice. When given external energy in the form of impact or heat, mercury occupying such irregular spots swings into irregular thermal movements unrelated with the lattice vibration of the crystal. This develops into a disrupting action of crystal lattices, and promotes the decay of the crystal, thence, the explosion. Mechanically speaking, this applies a type of leverage and promotes an exfoliating decay of atomic planes weak in bonding strength. Chemically speaking, it performs a catalytic action. In terms of the science of explosives, this means that the crude form of mercury fulminate is more sensitive to mechanical energy, ignites at lower temperatures in response to thermal energy, and has a wider range of dispersion than other forms. I have already explained in detail the fact that the so-called irregular spots of crystal have great bearing on the sensitivity of initial explosives.

4. The Effects of Crystal Impurities on the Ignition Point

In order to test the effects of impurities on the ignition point, 0.02 g of mercury fulminate of the white, crude and powder forms, respectively, was thrown into a test tube heated in a thermostatic metal bath maintained at 200 ± 0.5°C, and the time between the throw-in and the explosion was measured 50 times for each form of the sample. The dispersion of errors is shown in figure 8. The crude form and the powder form have shorter ignition times and wider dispersion, while the white mercury fulminate has a longer ignition time and a relatively small dispersion. Thus, we can clearly see the effect of impurities.

Temperature of metal bath: 200 ± 0.5°C
Measurements: 50 times

● Crude mercury fulminate
o Powder mercury fulminate
Δ White mercury fulminate
(Marks indicate the num-
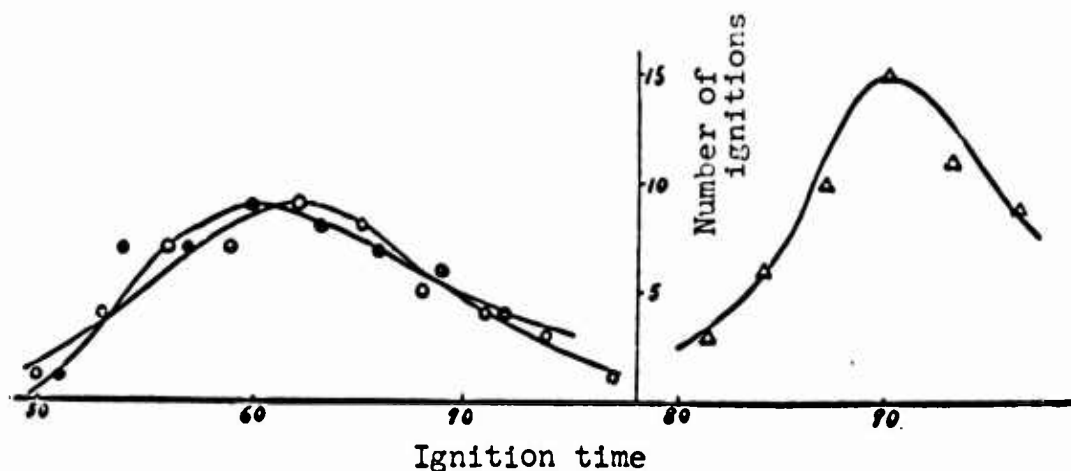ber of ignitions within
±1.5 sec)

Ignition time

Figure 8. Dispersion curves of ignition
times of the three forms of mercury
fulminate.

We can regard the interpretation of the role of impurities given in Sec-
tion 3 above as appropriate.

5.   Existence of Secondary Structure in
Mercury Fulminate

It is a matter of crystallographical common sense today that the
existing crystals are not ideal crystals, but that they have secondary
structures. This is also proved of mercury fulminate by an examination
of its Laue photographs. These photographs show thin Debye-Scherrer
rings besides Laue spots. This crystal, in addition to giving regular
Laue spots as the single crystal, gives Debye-Scherrer rings as if it
were a powdered sample, while the well-developed secondary structure
diffuses the Laue spots. The same phenomenon is observed in its rotary
crystal plane photographs.

6.   Dissimilarities in Crystal Structure between Mercury
Fulminate and Potassium Azide

The most important part of Garner's theory is the assumption that
the crystal structures of mercury fulminate and potassium azide are

similar, and that a simultaneous decomposition of two layers of fulminic ion of adjacent microcrystals is the cause of its explosion. In reality, it is rather a weak point of his theory. He pictured an image of the crystal of mercury fulminate by analogical inference alone, and based an important theory on his findings.

According to my analysis of the crystal structure of mercury fulminate, first, the bonding between mercury and the fulminic group in the molecule of mercury fulminate is little ionic and mostly molecular. Therefore, it is utterly wrong to consider the mercury ion layer and the fulminic ion layer to be independent of each other.

Secondly, there is no possibility of the two fulminic ion layers of adjacent microcrystals being in mutual contact. Therefore, we cannot regard as reasonable the theory that the simultaneous decomposition of these two layers is the cause of the explosion.

7. An Appropriate Image of the Explosion
   Mechanism of Mercury Fulminate

I tried to solve the foregoing contradiction and to picture a more rational image of pyrolysis and explosion mechanism. The thermal energy given externally flows along Smekal's cracks and, therefore, the thermal decomposition proceeds from the surface of each Smekal's block. In this case, the atomic planes parallel with the (010) plane, whose bonding strength is the weakest, decay and peel off first. The layers peeled off are considered to be in an unstable condition. Under additional thermal energy, these layers get separated into molecules. Of these liberated molecules, the activated ones begin to decompose. Mercury as generated from such decomposition is adsorbed onto the new layer after the decomposed layer. This new layer peels off under the heat to form an unstable layer, and its decomposition is promoted by activated mercury atoms on its surface that act as catalyst. In this way, the decomposition proceeds layer after layer. On the other hand, the number of mercury atoms that are generated from the decomposition and collect on the surface of the new layer increases, and inactive atoms increase as well. When the number of such inactive atoms collecting increases to a certain ratio to the new layer, they will interfere with the transmission of thermal energy to the new layer, and thus interfere with its decomposition.

I assume that the foregoing condition must be the one Garner pointed out about mercury fulminate after approximately 1/5 of it has decomposed. To verify this assumption, quantitative experiments must be conducted. It is assumed that, until approximately 1/5 is pyrolized, the (010) plane and the (100) plane, with the weakest bonding strengths, decompose simultaneously and generate a great amount of decomposition heat. This either triggers an explosion directly, or

causes a great number of new layers to decompose simultaneously and brings about an explosion. Furthermore, if the irregular spots existing for various reasons get in the act at any stage of the pyrolysis, this will overlap with the above-mentioned causes of explosion and actuate the explosion quite suddenly.

In the foregoing, I drew a most rational picture of the pyrolysis and explosion mechanism of mercury fulminate based on its crystal structure. This image of mechanism is also useful with respect to the explosion caused by a mechanical impact. I have already proved experimentally that in this case also the secondary structure of crystal plays an important role.

IX. QUANTUM-CHEMICAL CONSIDERATION OF EXPLOSIVE PROPERTIES OF INITIAL EXPLOSIVES

1. Electron Isosterism of Cyanic, Hydrozoic and Fulminic Groups

In order to discuss the explosive properties of initial explosives in terms of molecular stability, I consider the electron isosterism (ref. 43) of cyanic, hydrozoic and fulminic acids, and their metal salts.

According to the composition of ions of cyanic, hydrozoic and fulminic acids, their sums of atomic weights are 42 in all cases. The sums of electrons are 22 equally. Even though cyanates are not initiators, hydrozoates (azides) and fulminates of heavy metals are initiators. Thus, they are remarkably similar in molecular structure, on one hand, and remarkably different in nature, on the other. This is the very reason why I tried to explore the explosive properties using these three as subjects of study.

2. Comparison of Chemical Stability of Cyanic, Hydrozoic and Fulminic Acids

(1) Cyanic acid (ref. 44): A gas with an irritating odor and tearing property. Turns into a volatile liquid when cooled. It can be kept in the diluted solutions of ether, toluol, benzol and chloroform without changing in nature for several weeks. The more diluted its ice water solution is, the better it will keep. Above $0^{\circ}C$, its water solution rapidly decomposes into CO_2 and NH_3.

(2) Hydrozoic acid (ref. 45): Pure hydrozoic acid is a colorless and extremely volatile liquid, which boils at $37^{\circ}C$ and freezes at $-80^{\circ}C$. The water solution of this acid is a monobasic acid that can be maintained at a proper concentration. Most of its characteristics and reactions are remarkably similar to those of halogen acids.

(3) Fulminic acid (ref. 46): By cooling intensely, free fulminic acid can be kept in ether for several hours. Further, it can be volatilized without decomposition into a vacuum with ice cooled ether fumes. Therefore, it can be kept free in a gaseous form at low temperatures (approximately -50°C).

(4) Comparative considerations of stability of the three acids: According to literature, fulminic acid is chemically the most unstable, followed by hydrozoic acid. Cyanic acid is the most stable of the three. As fulminic acid is extremely unstable, its physical and chemical properties are not so well known as that of the other two.

3. Comparison of Thermochemical Properties and Crystal Structures of Potassium Salts of the Three Acids

(1) Comparison of thermochemical properties: Small amounts of potassium salts of the three acids are placed separately on the plate glass of a microscope and heated with a gas burner. Potassium cyanate soon begins to decompose. Potassium azide melts without decomposition. Meanwhile, potassium fulminate explodes loudly upon heating.

From this qualitative experiment, it is learned that, while the former two are relatively stable when heated, the latter is unstable. Furthermore, as electron diffraction photographs are being taken of the three potassium salts, potassium fulminate alone decomposes after approximately 2 minutes of electron radiation and the sample soon disappears. However, the other two are stable. This phenomenon constitutes also a fact to be considered in the comparison of stability.

Next, their melting points are measured.

Potassium cyanate begins to decompose at 220-230°C, but does not melt even at 250°C.

Potassium azide does not melt at 250°C, and is reported in literature to decompose in the vicinity of 355°C.

Potassium fulminate begins to decompose at 50-60°C and turns gray white. It explodes suddenly at 150°C.

(2) Comparison of crystal structures: By means of Debye-Scherrer X-ray diffraction photographs, I tried to prove in this study that potassium azide and potassium cyanate are isomorphic. Further, I took X-ray photographs of potassium fulminate, which has never been done before, and obtained interlattice plane distances.

Potassium cyanate		Potassium azide		Potassium fulminate	
Intensity	Lattice distance	Intensity	Lattice distance	Intensity	Lattice distance
10	2.81	10	2.79	4	2.87
5	2.63	2	2.62	2	2.72
3	2.38	2	2.40	1	2.35
3	2.21	2	2.19	1	2.16
5	1.97	5	1.99	1	2.08
3	1.80	10	1.79	1	2.05
3	1.70	5	1.72	2	1.99
2	1.65	2	1.66	3	1.93
3	1.51	6	1.55	2	1.78
2	1.41	2	1.41	1	1.74
3	1.37	5	1.38	2	1.61
3	1.33	2	1.34	4	1.58
3	1.30	5	1.31	2	1.52
1	1.28	2	1.26	1	1.48
5	1.13	8	1.14	7	1.42
5	1.08	5	1.08	5	1.38
5	1.00	5	1.01	4	1.36
2	0.99	2	0.99	1	1.31

According to the preceding table, we realize that potassium azide and potassium cyanate have extremely similar values, and that therefore they are isomorphic. As for potassium fulminate, values are obtained for the first time. They are not adequate to determine the structure of this potassium salt, but are sufficient to confirm that it is different from that of the other two.

4. Comparison of Initial Explosive Properties and Crystal Structure of Silver Salts of the Three Acids

(1) Comparison of initial explosive properties: Silver cyanate does not explode under heat or impact. When heated, it begins to decompose at approximately 150°C, and turns brown in the vicinity of 200°C.

Silver azide and silver fulminate are typical initial explosives. By measuring their ignition points and impact sensitivities, a comparison of their sensitivities as initial explosives can be made.

(a) Instantaneous ignition point:

Silver azide $352^{\circ}C$
Silver fulminate $225^{\circ}C$

From the above measurements, it is learned that silver fulminate has a lower ignition point than azide; therefore, it is more unstable under heat.

(b) Impact sensitivities: By the silver sand test, their unexplosive and explosive points were obtained.

	Unexplosive point (cm)	Explosive point (cm)
Silver azide	4	18
Silver fulminate	1 or less	8

Note: The falling weight for fulminate was 8.6 g and for azide 16.3 g.

Silver fulminate is markedly more sensitive to impact than silver azide.

(2) Comparison of crystal structures: Since the analysis of crystal structures of the three kinds of silver salts by X-rays is very difficult, hardly any such analysis has been conducted.

It was also impossible in the present study to make structure analyses. However, through the use of Debye-Scherrer X-ray photographs, distances between lattice planes were obtained for the first time and the fact that these three salts are not isomorphic was confirmed.

Silver cyanate		Silver azide		Silver fulminate	
Intensity	Lattice distance	Intensity	Lattice distance	Intensity	Lattice distance
3	4.53	2	4.29	10	5.00
3	4.13	4	3.65	2	4.53
1	2.84	1	3.42	2	3.83
3	2.72	3	3.28	10	3.49
10	2.65	3	2.84	1	3.31
10	2.57	3	2.70	1	3.25
1	2.48	3	2.56	1	3.10
1	2.43	10	2.33	1	2.99
3	2.33	2	2.05	1	2.90
1	2.28	9	1.99	1	2.81
1	2.25	3	1.81	1	2.73
10	2.21	3	1.74	8	2.61
2	2.10	7	1.64	8	2.55
2	1.98	7	1.55	10	2.48
2	1.88	7	1.50	10	2.21
2	1.83	1	1.47	1	2.10
5	1.74	9	1.38	1	2.02
2	1.65	1	1.34	10	1.93
1	1.63	1	1.31	10	1.91
1	1.60	2	1.30	8	1.84

5. Quantum-Chemical Consideration of the Results

In Chapter I, I described in detail the fact that Pauling had explained the explosive properties of azides by introducing the concept of quantum resonance into the molecular structure of azide ions. In the present study, I tried to expand on this to give quantum-chemical interpretation of the remaining two acid ions.

(1) The molecular structure and quantum resonance of cyanic acid ion: As the possible types of resonance for the cyanic acid ion, the following kinds can be considered

A $:\ddot{O} = C = \ddot{N}:$

B $:\ddot{\ddot{O}} - C \equiv N:$

C $:\ddot{O} \equiv C - \ddot{\ddot{N}}:$
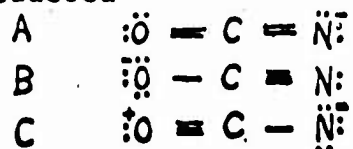
Now, the potential factor is fixed as follows

$$V(R) = \frac{1}{2}x_1 k_1 (R - R_1)^2 + \frac{1}{2}x_2 k_2 (R - R_2)^2 + \frac{1}{2}x_3 k_3 (R - R_3)^2$$

Here, x_1, x_2 and x_3 show the degrees of contribution made by the three types of structures to the molecular condition, and they are related to each other as follows: $x_1 + x_2 + x_3 = 1$. k is the bonding strength constant and R is the interatomic distance. The values of k in cases of single, double and triple bonds, respectively, are in the ratio of 1:3:6. The value of R in the equilibrium is obtained by fixing the value of the differential dV/dR at 0. Thus,

$$R = \frac{x_1 k_1 R_1 + x_2 k_2 R_2 + x_3 k_3 R_3}{x_1 k_1 + x_2 k_2 + x_3 k_3}$$

This means that R is a average of R_1 with $x_1 k_1$ as the weight. If we apply this formula to the cyanic ion,

$$R_1 = C—O = 1.43$$
$$R_2 = C=O = 1.22$$
$$R_3 = C\equiv O = 1.10$$
$$R_1' = C—N = 1.47$$
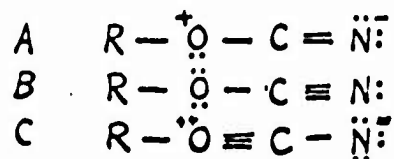$$R_2' = C=N = 1.27$$
$$R_3' = C\equiv N = 1.15$$

$$R = (\frac{1}{2} \times 1.43 + 1 \times 1.27 + 2 \times 1.10)/(\frac{1}{2} + 1 + 2)$$
$$= 1.17 \text{Å}$$

$$R' = (\frac{1}{2} \times 1.47 + 1 \times 1.27 + 2 \times 1.15)/(\frac{1}{2} + 1 + 2)$$
$$= 1.22 \text{Å}$$

Next, we consider the following three kinds as the possible types of covalent bonding molecule. These do not violate the rule of adjacent charges.

A $R - \overset{+}{\underset{..}{O}} - C = \overset{..}{\underset{..}{N}}:$
B $R - \overset{..}{\underset{..}{O}} - C \equiv N:$
C $R - \overset{..}{\underset{..}{O}} \equiv C - \overset{..}{\underset{..}{N}}:$

In his study of crystal structure of KN_3 and KOCN by X-rays,

Pauling decided these two were isomorphic, and gave the same value to

the interatomic distance between O-C and C-N of KOCN as that of N-N of KN$_3$. By changing the degrees of contribution of the above three struc-

tures, A, B and C, I tried to bring the value of N-N to Pauling's, but did not succeed. Further, there is nothing wrong with assuming that A, B and C make an equal degree of contribution. The validity of this method of calculation is supported by the fact that, when the inter-atomic distances of carbon oxysulfide COS and nitrous oxide N$_2$O were

calculated by this method, the calculated values agreed with the meas-ured values. Therefore, KOCN, with interatomic distances of C-O = 1.17Å and C-N = 1.22Å, can be isomorphic with KN$_3$ and the atomic distance of N-N = 1.15Å.

(2) The molecular structure and quantum resonance of the fulminic acid ion: The possible types of resonance for the fulminic acid ion are

$$
\begin{array}{ll}
A & :\ddot{O} = N^r = \ddot{C}: \\
B & :\ddot{O} - \dot{N}^* \equiv C: \\
C & :O \equiv N^r - \ddot{C}:
\end{array}
$$
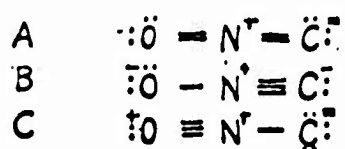
Structure C violates the rule of adjacent charges, and must be elimi-nated. If we assume the remaining two structures, A and B, make the same degree of resonance,

$$
\begin{aligned}
R_1 &= O-N = 1.36 \\
R_2 &= O-N = 1.15 \\
R_1' &= C-N = 1.27 \\
R_2' &= C \equiv N = 1.15 \\
R &= (\tfrac{1}{2} \times 1.36 + 1.15)/(\tfrac{1}{2}+1) = 1.20\text{Å} \\
R' &= (1.27 + 2 \times 1.15)/(1+2) = 1.19\text{Å}.
\end{aligned}
$$

Thus, the interatomic distance of the left half of ONC$^-$ is about equal to that of the right half.

A quite interesting fact is that KONC which is symmetrical in terms of interatomic distances of acid ion is not isomorphic, and that KOCN, which is not symmetrical, but has a relatively similar inter-atomic distance on one side, is isomorphic with KN$_3$.

As for the fulminic group, the following two structures of covalent bonding molecule are considered

$$
\begin{array}{ll}
A & R - \dot{O} = N^* = \ddot{C}: \\
B & R - \ddot{O} - N^* \equiv C:
\end{array}
$$
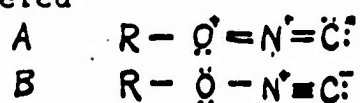
However, A violates the rule of adjacent charges, making resonance impossible. B is the only possible structure.

(3) The stability and quantum resonance of potassium salts of the three acids: The potassium salts of the three acids are almost perfectly ionic bonding compounds. Therefore, the number of ionic resonances is 3 for potassium azide, 3 for potassium cyanate, and 2 for potassium fulminate. A small number of quantum resonances means a small amount of resonance energy, hence, a small degree of stability as a compound. The fact that, of the three potassium salts, potassium fulminate is the most unstable under heat, and the fact that potassium azide is far more stable than was expected, can be explained as due to the number of quantum resonances and, by the same token, the amount of resonance energy.

(4) The explosive properties and quantum resonance of silver salts of the three acids: Contrary to the potassium salts, the silver salts of the three acids are almost perfectly covalent bonding compounds. Therefore, the numbers of resonances of these three acid radicals correspond with those for covalent bonding molecules. Therefore, the number is 2 for silver azide, 3 for silver cyanate, and 1 for silver fulminate. As opposed to silver azide and silver fulminate that have one less number than their potassium salts, silver cyanate has the same number. Silver cyanate has no explosive properties, and is not remarkably more unstable than its potassium salt.

On the other hand, silver azide and silver fulminate are typical initial explosives. They show a phenomenal unstability under heat and mechanical impact, which feature was hardly noticeable with their potassium salts. This outstanding fact is entirely attributable to whether the number of quantum resonances decreases or not. The greater sensitivity of silver fulminate than of silver azide is ascribed to the smaller number of resonances of the former, namely 1, than that of the latter, namely 2; thence, smaller amount of resonance energy.

Now, I will show about azides how much of the resonance energy decreases with the decrease of number of quantum resonances. According to Pauling's calculation method (ref. 47), the resonance energy among three structures is about 45 kcal/mol; the resonance energy between two structures is about 25 kcal/mol. In other words, the covalent type is about 20 kcal/mol more unstable than the ionic type.

Next, I will examine the relationship between heat of formation and the unstabilization due to the decrease of reasonance energy. As for silver fulminate,

$$[AgONC] = [Ag] + (CO) + 1/2(N_2) + 70.5 \text{ kcal (ref. 48)}.$$
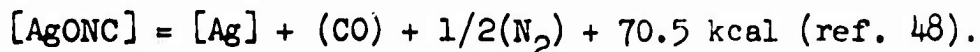
If we assume silver cyanate decomposes the same way,

$$[AgOCN] = [Ag] + (CO) + 1/2(N_2) + 4.0 \text{ kcal.}[1]$$

The difference in heat of decomposition between the two is 66.5 kcal.

Meanwhile, the difference in resonance energy between silver cyanate and silver fulminate is 45 kcal, if calculated in the manner azides were calculated. The difference in stability between the only possible bonding type of silver fulminate and the corresponding bonding type, namely B, of silver cyanate is considered to be about 20 kcal.[2] The sum of these two is 65 kcal. This value is roughly in accord with the value of the difference in heat of decomposition given above. This is evidence that unstability can adequately be explained by the decrease of quantum resonance energy.

(5) Unstabilization and quantum resonance numbers of the three acids and their salts: By summarizing the foregoing discussion, the relationships between unstability and quantum resonance numbers of the three acids and their salts are shown in the following table.

		Cyanic	Hydrozoic	Fulminic
Free acid	Stability	great	little	minimum
	Quantum reso-nance number	3	2	1
Potassium salt	Stability	great	great	little
	Quantum reso-nance number	3	3	2
Silver salt	Stability	great	little	minimum
	Quantum reso-nance number	3	2	1

X. SUMMARY

1. In the low temperature range, the change of sensitivity of the three forms of mercury fulminate and lead trinitroresorcinol by temperature is roughly linear. Therefore, of the two theoretical formulas showing the change of sensitivity by temperature, Arami's has more universal validity over a wider range of temperatures than Taylor's.

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[1] $[Ag] + [C] + 1/2(N_2) + 1/2(O_2) = [AgOCN] + 23.1$ kcal (ref. 49).

[2] That is, the difference in stability between the two can mainly be ascribed to the difference in energy between the single bonds of O-N and O-C. The bond energy of O-C is 70.0 kcal (ref. 50). No value of this kind of energy has been obtained for O-N. However, from various data, it is assumed to be approximately 50 kcal.

2.   We obtained ignition time lags of various initial explosives at various temperatures, and calculated activation energy from these. Knowing these values, we confirmed that there are two types of initial explosives, namely the lead azide type and the mercury fulminate type. These results agree with those M. Patry obtained by chronograph.

3.   Regarding the ignition of initial explosives, we measured the effects of bridge current amperages and bridge lengths by changing them, respectively.

4.   We examined K. Drekopf's theoretical formula, and clarified the fact that it has merely qualitative significance.

5.   We found that initial explosives can be classified into the following three categories according to the relationship between spark impulse and current amperage: /161

    (1) those whose spark impulse decreases as ignition current decreases;

    (2) those whose spark impulse remains the same regardless of ignition current;

    (3) those whose spark impulse increases as ignition current decreases.

6.   As a result of obtaining spark impulses of various initial explosives, we quite accidentally came to endorse Patry's reasoning, adding a new fact.

7.   We found out that lead trinitroresorcinol has an outstanding characteristic when ignited by an electric bridge. It has a strikingly small spark impulse in spite of a high ignition point and great activation energy.

The reason for this fact was explored from the viewpoint of molecular structure by comparing it with lead picrate. It was concluded that the straight chain bond molecular structure of lead trinitroresorcinol is unstable under external energy being applied instantaneously and locally.

8.   By introducing for the first time the concept of the irregular spots and the secondary structure of crystallography into the study of sensitivity of initial explosives, we explained the differences in sensitivity existing among the various forms of mercury fulminate, and the relationship between the grain size and sensitivity of lead trinitroresorcinol.

9. We proved the existence of irregular spots and a secondary structure in mercury fulminate by making the following experiments:

(1) microscopical observation of a single crystal;

(2) microscopical pursuit of changes of white mercury fulminate crystals while heating;

(3) X-ray pursuit of changes of crude mercury fulminate crystals while heating;

(4) observation of the explosion of white mercury fulminate crystals by instantaneous heating;

(5) microscopical and X-ray observations of collapse of crude mercury fulminate crystals by pressure filling into a detonator.

10. Using Weissenberg's X-ray goniometer and Bragg's ionization spectrometer, we analyzed the crystal structure of mercury fulminate. The space group is D_{2h}^{15}, and mercury forms a face-centered cubic lattice. The position of the fulminic group could not be determined, as it is overshone by mercury.

11. As for the position of the fulminic group, we assumed a most probable one by drawing on the concept of quantum resonance.

12. Based on the obtained image of the crystal of mercury fulminate, the following items were examined:

(1) the plate shape form of the crystal of mercury fulminate;

(2) the fact that the crystal of mercury fulminate easily cracks in the direction of axis c;

(3) the position occupied by impurities in the crystal of crude mercury fulminate;

(4) the effects of impurities in the crystal on the ignition point;

(5) the existence of the secondary structure in mercury fulminate;

(6) the dissimilarities in crystal structure between mercury fulminate and potassium azide;

(7) an appropriate image of explosion mechanism of mercury fulminate.

13. We examined the chemical stability and sensitivity of three isosteric acids: cyanic, hydrozoic and fulminic acids, and their metal salts. The results are summarized as follows:

(1) Of the three acids, fulminic acid is the most unstable.

(2) Of the three potassium salts, potassium fulminate is the most unstable. It has explosive properties. It was found out that it explodes when radiated with electrons.

(3) Of the three silver salts, silver azide and silver fulminate have explosive properties, and can be used as initial explosives. Silver fulminate is by far the most sensitive, and has a low ignition point.

14. We studied quantum resonance numbers of the three acids and their metal salts. Their quantum resonance numbers and degree of unstability are shown below.

		Cyanic	Hydrozoic	Fulminic
Free acid	Stability	great	little	minimum
	Quantum resonance number	3	^	1
Potassium salt	Stability	great	great	little
	Quantum resonance number	3	3	2
Silver salt	Stability	great	little	minimum
	Quantum resonance number	3	2	1

This study report has been compiled by extracting important parts from "Physical and Chemical Studies of Initial Explosives" which I submitted to the Science Department, Tokyo University, in December 1964, as the thesis for the obtention of a degree. (Explanations referring to microscopic photographs and X-ray photographs constituted the bulk of the thesis, but I omitted these here.) I regret that I failed to publish this until today, as I have been quite busy meeting the demands of day-to-day business since the end of the war. In retrospect, the thesis was written in stirring times of the war, while I was engaged in the study of explosives and pyrotechnics. Many experiments and theories contained in it are far from satisfactory today.

I express my profound appreciation to my respected teacher, Dr. Sabuichiro Mizushima, professor at Tokyo University, for his great assistance in this study. Further I thank Prof. Ito and Asst. Prof. Sawada of the Mineralogical Laboratory, Science Department, Tokyo University, for allowing me to use the facilities for crystal analysis, and giving me useful advice about the method of analysis. Also, Dr. Naruto Yamaguchi, my friend, gave me useful advice. In the former Imperial Navy, Mr. Motoji Nomura (then Maj. Gen., Technical Corps) gave me various assistance in the study. Mr. Kaname Shiihara (then Capt., Technical Corps) assisted me in the synthesis and preparation of samples. I hereby express my gratitude.

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